

Enhancing Packaging Materials: A Microstructural Investigation of Graphene Dispersion on Polymer Surfaces

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Graphene is a versatile constituent with many applications in novel materials demanding improved electrical conductivity and mechanical resistance. Another application reported in the literature is its use as a barrier agent to gases, lipids, and water vapor, due to its honeycomb basal structure. We report on a straightforward method to achieve the surface modification of different substrates by depositing a graphene dispersion. The graphene dispersion in N-methyl-2-pyrrolidone (NMP) was prepared by liquid-phase mechanical exfoliation of graphite flakes and characterized to be comprised by multilayer graphene (mG). Ordinary commercial substrates, films produced by the packaging industry, such as low-density polyethylene (LDPE), poly(ethylene terephthalate) (PET), paper, and cellophane (CEL) were treated by a mG dispersion using drip casting. Scanning electron microscopy (SEM) was carried out on these different substrates before and after mG coating. LDPE showed irregular mG covering and aggregation, compared to the uniform distribution in PET and cellophane films, that corroborates the results obtained from tape tests. UV-Vis transmittance indicated minimal interference from the graphene layer compared to the uncoated film. The results were discussed taking into account the interplay of the surface energy of the chemical substances involved. The different modified films might work as a barrier packaging films.

Keywords: *Graphene, barrier, surface energy, coating.*

1. Introduction

Due to their versatility, ease of processing and low density, a wide range of polymers is used in food, hygiene, anti-corrosion, and health products' packaging. Among these polymers, we can highlight the most common, polyethylene, which is easy to process, low cost, food safe, but does not serve as a barrier to gases, lipids, and water vapor at desirable levels¹.

To improve the barrier properties, for instance, the industry uses the coextrusion of polyethylene with polymers such as polyamide, made compatible *in situ* through coextrusion adhesives. Another way to improve barrier properties is to combine the polymeric film such as in metallized polymer film or apply an aluminum coating²⁻⁴. Thin films of strong, modestly flexible metals such as aluminum form excellent barriers, but the presence of defects during stretching, bending, and handling limits their use. The packaging industry continuously seeks materials and processes to preserve the key features of the wrapped goods, in addition to achieve improved mechanical, optical, and chemical properties according to eco-designing principles, summarized as the 4 R's: reduce, reuse, recycle and repurpose. Graphene is a versatile 2D material that, due to its dense honeycomb structure and its sp²-bonded carbon atoms, has been reported to present remarkable properties, exemplified by its electrical and thermal conductivity, mechanical strength and fluid diffusion⁵, its good thermal stability, antibacterial properties,

and chemically inertness^{6,7} endorse its application in food packaging and protecting industry. In addition, even used as filler or coating in plastics a barrier across the film is formed, as permeation of gases and water vapor is obstructed by the dispersed platelets with honeycomb structure that create tortuous paths on the substrate's surface or within the substrate¹. Nonetheless, the high surface area of this allotropic form of carbon provides higher barrier properties compared to other types of particulate barrier materials, such as silica⁸.

To obtain good barrier properties, the graphene-polymer systems need to present uniform graphene dispersion in the polymer matrix or, a homogeneous graphene coating onto the polymeric material. Graphene presents low affinity with common polymers, whereas graphene oxide has functional groups that improve the interfacial bondings¹.

Casting requires wettability of the polymer surface by the graphene dispersion, although plastic films could undergo surface pretreatment which is not uncommon in packaging industry. Graphene presents excellent conductivity⁹, so an extra antistatic protection especially for the powder products.

Homogeneous and stable dispersion of graphene are essential to achieve well-coated substrates by casting. The mechanical exfoliation of graphite in liquid phase is one of the successful methods to prepare well-dispersed graphene with good control of defects.

Liquid-phase exfoliation of natural graphite, which is inexpensive and available in large quantities, is an efficient way to produce few defects graphene¹⁰ in a scalable way

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at low-cost¹¹. In general, graphite together with a liquid medium and an energy source for supporting exfoliation are successfully employed to separate the graphene sheets, linked by van der Waals bonds¹².

N-methyl-2-pyrrolidone (NMP) is a highly effective solvent for exfoliating graphite aiming to graphene, due to their strong interaction or low energy required for exfoliation and subsequent solvation, expressed as matching in terms of Hansen solubility parameters, δ_D (MPa)^{1/2}, δ_P (MPa)^{1/2} and δ_H (MPa)^{1/2}, reported as 18, 12.3 and 7.2 for NMP, and 18 (15-21), 9.3 (3-17) and 7.7 (2-18) for graphene¹³. However, NMP removal is difficult due to its high boiling point. Excess of solution, and consequently, excess of graphene can also cause it to aggregate, making its deposition poorly distributed. Other factors such as surface treatment, defects in the polymeric substrate and rheological characteristics also influence the compatibility and the distribution of graphene on the polymeric surfaces¹⁴, besides agglomeration and stacking may occur mainly driven by the weak van der Waals bonds, quite usual in the preparation of polymeric nanocomposites^{2,15}.

In this work, the multilayer graphene (mG) was prepared via mechanical exfoliation in liquid phase from pristine graphite in NMP, which facilitates an easy casting on substrates, such as polymer films and paper used in the packaging industry. The morphology of the mG coatings on the different substrates were observed by SEM. The features of the coated substrates are diversified, and the results are consequences of the physicochemical interactions among the constituents during the coating formation. We explain the observed morphology taking into account the role of the surface energy of the substrate and mG and the surface tension of NMP.

2. Experimental

2.1. Preparation of the multilayer graphene dispersion (mG)

Multilayer graphene dispersion (mG) is prepared via liquid phase exfoliation¹⁰. 9g of pristine graphite flakes (99.6% min., Nacional de Grafite LTDA.) were mixed with 50mL of NMP (99.8% min., BASF), then the mixture was heated in a silicone oil bath at 200 °C for 20 hours, cooled and filtered. The precipitate was washed in a mixture of 150 mL of distilled water and 100 mL of absolute ethanol and dried in a vacuum oven at room temperature. 400 mL of NMP was added to 4g of this expanded graphite, forming a dispersion at 10mg/mL. The mixture was kept for 200 hours in an ultrasonic bath (Quimis Model Q335D, 135W RMS), then centrifuged and the supernatant was vacuum filtered through a 0.7 µm-pore size membrane. The resulting dispersion of mG in NMP was kept under refrigeration and taken to room temperature before use.

2.2. Packaging films

Ordinary films from the packaging industry were selected, namely: low-density polyethylene (LDPE, 0.02mm thickness, Lafra Plásticos), cellophane (CEL, 0.01 mm and 0.02mm thickness, Celofilme Filmes), and poly(ethylene terephthalate)

(PET, 0.02mm thickness, Pratsy Embalagens). In addition to plastic materials, ordinary printing and writing paper (75 g/m², 0.07mm thickness, International Paper) was chosen to analyze the coating on irregular and porous surfaces.

2.3. Preparation of films with mG

The polymer films and paper samples were cut into a square shape with approximately 4 cm length. On a flat and level surface, the samples were placed in Petri dishes and 0.4 mL or 0.8 mL of the mG in NMP was dripped on the samples' top. For CEL and PET, 0.4 and 0.8 mL of this solution were dripped on top of them. The samples were dried for 24 hours in an oven with ventilation at 40° C for LDPE and 50° C for other substrates. NMP was chosen as a solvent to maintain stable graphene dispersion and prevent damage to these specific polymer films.

2.4. Raman spectroscopy

Raman spectroscopy was performed on a WITec Confocal Raman Microscope (model Alpha 300R) using 532 nm (green) laser, with a maximum power of 45 mW. The laser power was reduced to 8mW in order to preserve the polymer samples. Samples of pristine graphite, graphite after thermal expansion, retained graphite on the membrane filter (>0.7 µm) and graphene film deposited on a glass slide by spin-coating were analyzed. The films were prepared at 500 rpm/20s, using a spin-coater (Swin 4" Table Top Economic Coater, model EC4 SYN 3S102-0902) connected to a vacuum pump (Yung -I Co. Ltd., model T-33), and dried on a heating plate (Yotec, model YS-200S) at 120°C/20 min. The ratios between the intensities of the characteristic bands due to the graphitic structure and defects (I_D/I_G and I_{2D}/I_G) were determined. The position, shape and height of the peaks were analyzed to get information about the structure and defects of the graphene produced. Peak deconvolution using Origin 8® was performed to assist the analysis.

2.5. Scanning Electronic Microscopy (SEM)

Samples were fixed with silver glue on the SEM specimen stubs and coated with gold prior to analysis. A FEI scanning electron microscope (model Inspect F50) was used to examine the features of the coatings, at accelerating voltage of 2.00 to 10.00 kV and working distance of 10 to 12 mm. Images were acquired using a SE detector and magnifications from 1000 to 50000 X.

2.6. Ultraviolet-Visible Spectroscopy (UV-Vis)

Transmittance spectras were collected using an Agilent Cary 50 Spectrophotometer. Samples were fixed in a solid film holder and analyzed between 200 to 800 nm, in a dual beam mode with data capture at interval of 1 nm.

2.7. Coating adhesion

Interfacial adhesion of multilayer graphene thin films to PET, CEL, and LDPE polymeric substrates was evaluated using a 19 mm wide pressure-sensitive adhesive tape test, conducted in accordance with ASTM F2252/F2252M-13. Following application and subsequent removal of the tape from mG-coated specimens, both the tape and substrate surfaces were meticulously examined for evidence of graphene

transfer. This qualitative analysis provided an assessment of the compatibility between the graphene coating and the substrates.

3. Results and Discussion

Pristine graphite was exfoliated by subjected to heat-pretreatment in NMP at 200 °C, enabling NMP molecules to diffuse within the graphite flakes, between the graphene layers, fostering their separation by ultrasonication. The dispersion formed is very stable and after more than 2 years, there is no visually observable precipitation (Figure 1). It is well-known that one of the main challenges is to produce homogeneous stable liquid-phase exfoliated graphene¹⁰. Sample concentration was quantified after specimens were dried until a constant mass was achieved, and the residual solid mass was determined, resulting in a solute concentration of 5.25 ± 0.35 mg/mL.

Before characterizations by Raman spectroscopy and the coating experiments, a pre-established volume of dispersion of the mG in NMP was placed in an ultrasonic bath for 3h, in order to minimize any discrete aggregation.

3.1. Raman spectroscopy of graphite and mG

Figure 2 shows the spectra of pristine graphite and graphene film on glass. The spectra of thermally expanded graphite and graphite retained after filtration were suppressed, as there was no noticeable change compared to pristine graphite. In both spectra, the characteristic peaks of graphitic materials are present, with their positions highlighted.

Sp²- carbon atoms at the edge of graphene sheets, those that do not have a zigzag or ring alignment in the presence of a vacancy are responsible for the existence of the D peak¹⁶, that is, it requires defects to be activated¹⁷. Peak D shows a Raman shift of about 4 cm⁻¹ in the mG spectrum, in relation to its position in the pristine graphite spectrum, changing from 1342 cm⁻¹ to 1346 cm⁻¹. The stretching of the C-C bonds of the sp²- carbon atoms in the hexagonal basal plane produces the G peak, located near 1579 cm⁻¹ in both spectra. The vibration of second-order D phonons produces the 2D band¹⁸. The shift of this band, located at 2717 cm⁻¹ in the spectrum of the pristine graphite, to 2685.7 cm⁻¹ (displacement of about 33 cm⁻¹) in the spectrum of graphene indicates a reduction in the number of layers in the material). The change in the band shape is also an indication of the transformation from graphite to graphene¹⁹. A 2D band that is wide in relation to the G band is evidence of few-layer graphene, although the band becomes narrow again for monolayer graphene, but shifted to lower wavenumber compared to graphite²⁰. The 2D peak is the second order of the D peak and is composed of a single peak for monolayer graphene, which can be deconvoluted into four peaks for bilayer graphene, for example, due to the evolution of the electronic band structure²¹. The D' peak results from a double resonance process and is located close to 1620 cm⁻¹. It is noted that this peak is not visible in Figure 2, but the existence of the 2D' peak, which is the second order of peak D', shows that D' is present. It should be emphasized that D and D' are present in samples with defects, while the 2D and 2D' peaks are independent of the existence of defects and always appear in the spectrum, since they originate from a process with



Figure 1. Stable dispersion of mG in NMP.

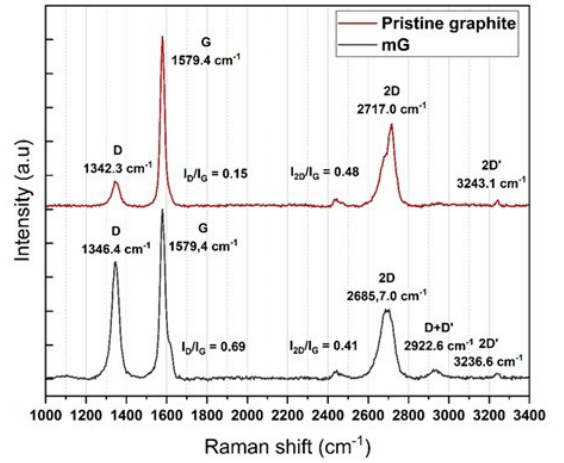


Figure 2. Raman spectrum of pristine graphite and mG.

conservation of momentum, resulting from two phonons with opposite wave-vectors. The D+D' band, present only in the mG spectrum, results from the combination of phonons with different momenta, so its occurrence can be associated with the presence of defects¹⁷.

The ratios between the intensities of the D and G peaks (I_D/I_G) and of the 2D and G peaks (I_{2D}/I_G) for both spectra can be seen in Figure 2. I_D/I_G is inversely proportional to the size of the graphitic crystallite, when the defects are armchair edges on graphene and not vacancies inside the hexagonal basal plane¹⁸. I_D/I_G can also be associated with disorder in carbon materials²¹, so that the increase from 0.15 in pristine graphite to 0.69 in mG points to an increase in disorder in the second material or a reduction in the particle sizes. The armchair edges on graphene sheets appear in Raman spectroscopy as defects, that is, greater amounts of smaller-sized graphene led to a greater amount of defects²², increasing the intensity of D. In the literature^{23,24}, the ratio I_{2D}/I_G is used to estimate the number of layers of graphene. For mono, bi and few-layer graphene the values of I_{2D}/I_G are 3.31, 1.56 and 0.54, respectively, so that the graphene mG studied here can be classified as few-layer graphene ($I_{2D}/I_G = 0.41$).

Figure 3 shows the deconvolution of the D, G and 2D peaks as Lorentzian functions. Figure 3a shows that it is possible to decompose the D peak of pristine graphite into two components D1 and D2, while for mG (Figure 3d) there is a single peak, showing that in addition to being more intense, it has become narrower. In pristine graphite, D1 has a higher intensity compared to D2. The decomposition into two peaks is consistent with the literature¹⁹. Figures 2b and 2e show that in the case of the G peak, although pristine graphite has a thinner peak, the deconvolution is possible for both pristine graphite and mG, revealing the aforementioned D' peak, indicating the existence of amorphous defects¹⁷. It should be emphasized that the D' band is smaller in the pristine graphite spectrum, but its existence is assured by the 2D' band (3243.1 cm^{-1}), as mentioned before. Figure 3c shows the deconvolution of the 2D band of pristine graphite into two peaks, while mG into four peaks (Figure 3f). Additionally, the shape of the 2D band changes, the 2D of mG is broader indicating existence of additional components. The band shift to lower wavenumber, as already mentioned, can be seen once again. For pristine graphite, the 2D band is commonly decomposed into 2 components¹⁹, but for graphene, the decomposition varies according to the number of layers. For monolayer graphene, the 2D band is composed of a single peak, while for bilayer graphene, it can be decomposed into 4 components¹⁹ reaching more components for graphene with more layers, also depending on the laser wavelength²⁵, and the order of stacking, ABA versus ABC, of these few layers²⁶. When 2- to 5-layer graphene is excited by a 633 nm laser, the 2D band exhibits larger shift to lower wavenumber and larger broadening compared to the 2D band observed at 532 nm. Furthermore, it is noteworthy that for graphene with more than 5 layers, the spectrum in this range becomes very similar to that of pristine graphite¹⁹, thus the features observed in Figure 3f indicate that the graphene obtained in this work may represent a set of graphenes having 2 to 5 layers.

3.2. Deposition of mG on the surface of the polymers

For the majority of polymer substrates, drip coating by mG showed good spreading by visual inspection. Table 1 shows the results of the mG coating on the films. The table also shows the volume of dispersion applied and the oven time used to ensure evaporation to dryness, visual aspects, and UV-Vis transmittance results.

Uniform coatings were observed on the non-polyolefinic films, while for the LDPE, there were regions with high concentration of graphene and regions without coverage. This is due to the repulsion between the polar dispersion and the substrate. Costa et al.¹⁴ indicated that the poor visual aspect of the films is consequence of the high values of surface tension between graphene and polyethylene and polypropylene, though graphene coating was carried out using chemical vapor deposition (CVD), additionally, on polar surfaces of polymers such as polyvinylidene fluoride (PVDF), graphene coating was essentially uniform.

UV-Vis spectra showed similar results for all samples in the visible range, with a small difference for LDPE-coated graphene, corroborating the visual observations (Figure 4).

The transmittance results exhibited high values across all samples, including those with LDPE substrates featuring a suboptimal coating, thereby demonstrating the potential of graphene as a viable alternative for plastic film coating. Furthermore, the uncoated polymer films also yielded elevated transmittance values, indicating a minimal influence of the graphene film coatings.

3.3. Scanning Electron Microscopy

The samples' surfaces were analyzed by SEM before and after treatment with mG. LDPE has shown low wettability by mG dispersion by drip casting, and agglomeration of the mG particles occurred during the slow evaporation of NMP. The formation of a uniformly spread film of mG

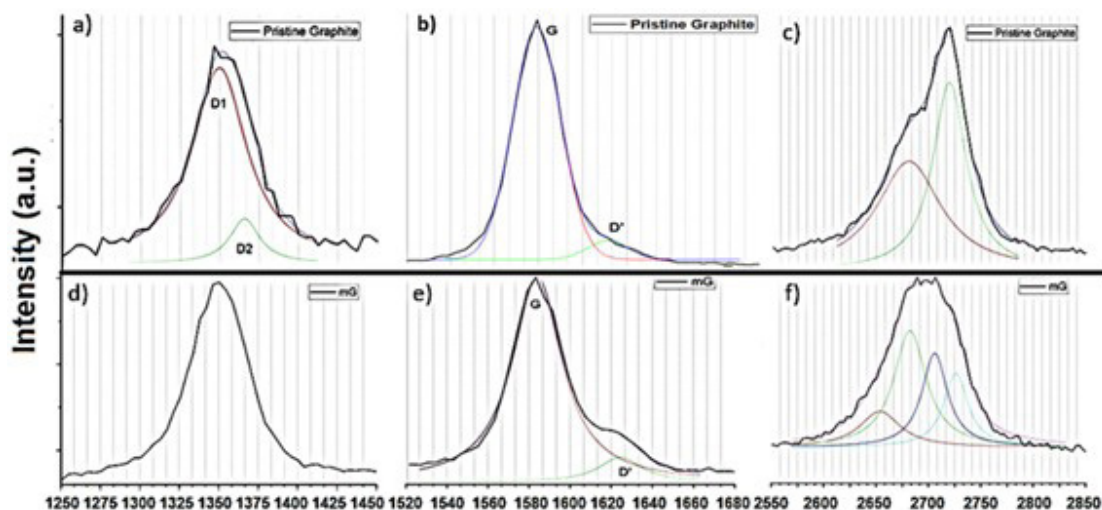
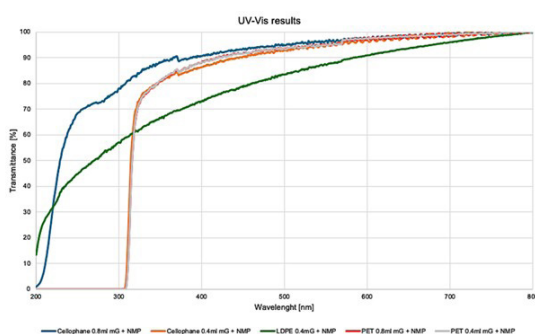


Figure 3. Comparison of D, G and 2D bands of pristine graphite and mG: a) D peak of pristine graphite decomposed into D1 and D2; b) G peak of pristine graphite decomposed into G and D'; c) 2D band of pristine graphite decomposed into 2 components; d) D peak of mG; e) G peak of mG decomposed into G and D'; and f) 2D band of mG decomposed into four components.

Table 1. Results observed for films treated with graphene dispersion.

Material	Volume of mG dispersion (ml)	Oven time (h)	Visual aspects of the coating after drying in the oven	% Transmittance at 550 nm
LDPE	0.4	48	Non-uniform coverage, with points of higher concentration of graphene and reduced transparency at these points.	88
CEL	0.4	48	Uniform coating with little change in film transparency.	96
CEL	0.8	48	Uniform coating with little change in film transparency.	97
PET	0.8	48	Uniform coating with little change in film transparency.	96
PET	0.4	48	Uniform coating with little change in film transparency.	96
paper	0.4	24	Change in the color of the paper from white to gray. Dispersion was absorbed by the porous material.	Not applicable

**Figure 4.** UV-Vis spectra of graphene coated films.

did not take place, indicating grim perspective for its use as a barrier agent in packaging without previous proper surfacing. It is important to highlight that HDPE, LDPE and LLDPE are the most widely used packaging materials, utensils, and containers, due to its lightness, low-cost, easy fabrication along with good mechanical properties and water-resistance. Thus, new research focused on PE surface modification to improve its barrier properties can be promising, especially through simple new materials and techniques. LDPE presented mG submicron particles with globular morphology (Figure 5a) interconnected into much larger quasi-continuous bidimensional sheets (spots). The quantitative analysis showed that the average globules diameter is $0.6 \pm 0.1 \mu\text{m}$ and ca. 32 ± 3.39 globules per $25 \mu\text{m}^2$. The formation of solid globular particles from liquid phase is rather usual during evaporation process when sol-gel equilibrium takes place to reduce interfacial contact. Graphenes tend to rearrange due to its huge specific surface area, and the van der Waals force between the layers, and in this case, we believe, the repulsive forces between substrate and dispersion medium and the homogenous sizes of the mG sheets contribute to their auto-assembling into these uniform-sized mG spheres. However, leaves and some globules were also seen in the poorly dispersed deposition (Figure 5b). Pristine LDPE is also shown for comparison (Figure 5c); a fibrillar microstructure (Figures 5b and 5c) is

apparent and results from the preferential chain orientation during transformation/processing to the resultant LDPE film.

In fact, although composite nanoparticles of metal and metal oxides containing graphene forming micron-sized particles have been studied before^{27,28} such submicron pristine globular graphene is rather uncommon, thus we are aware of only one publication in shungite carbon, a natural carbon allotrope with applications in biomedicine, catalysis, and material science²⁹. There is another paper describing such structure in pristine graphene produced by Ningbo Institute of Chinese Academy of Sciences, where globular particles present wide distribution of particle sizes in the range of 10–100 μm ³⁰. However, there are also some reports on much smaller graphene particles, units to few tens of nm quantum dots³¹, which are described to provide submicron graphene particles having hydrodynamic radius from ca. 100nm to ca. 700nm, accomplished via aggregation of graphene quantum dots (GQD) in various liquid media³².

In contrast to LDPE, CEL and PET exhibit superior wettability when interacting with mG dispersion, demonstrating consistent and even spreading characteristics. This corroborates the qualitative results obtained from the adhesive tape tests and the surface energy values. The surface energy of LDPE is ca. 31 to 33 mN/m, while PET, ca. 42–43 mN/m and cellulose ca. 54.5 mN/m, compared to the surface tension of NMP, 43.8 mN/m³³. The surface energy of graphene is a complex issue, as it changes according to the preparation method, number of layers, roughness, types and number of defects, among the primary variables. However, for graphene sheets produced by chemical exfoliation of natural graphite flakes, followed by chemical reduction, values of surface energy have been estimated in the range 46.7 to 62.1 Nm/m³⁴. Additionally, for few-layer graphene produced by mechanical exfoliation of graphite, modeling data suggest a surface energy of graphene of $\sim 68 \text{ Nm/m}^35$.

After drying, the mG sheets are evenly distributed over the CEL surface; however, they do not remain oriented parallel to the surface. Instead, they are positioned at several upright angles, resembling a layer of autumn leaves scattered on the ground (Figure 6a). This covering of large number of leaves presents narrow trails and high surface area that delays and/

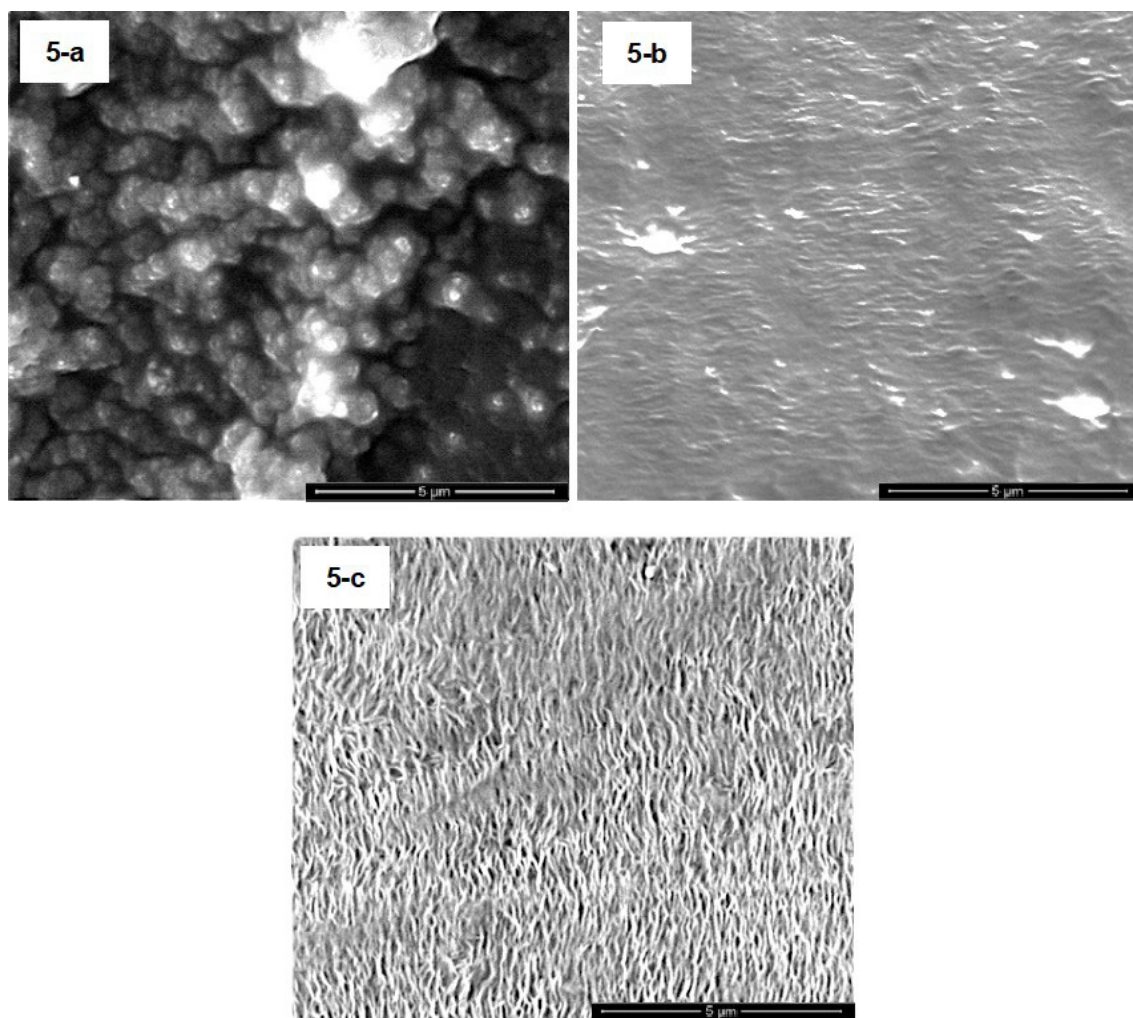


Figure 5. SEM images of LDPE (25000X): a) with globular graphene aggregation; b) graphene poorly dispersed; and c) without any coating.

or prevents the passage of agents such as moisture, water vapor, oxygen, and lipids. Besides, the connection between the leaves also helps to dissipate potential electrostatic charges build up on the surface of the substrate and this kind of coating may also throw out and dissipates the heat produced under the substrate. PET and CEL exhibit large regions uniformly covered with mG. CEL shows mG covering uniformly its surface, creating a physical barrier (Figure 6). It is possible to see that the leaves are not flawlessly parallel to the substrate surface. A quantitative analysis of the leaves sizes on the cellophane surface showed an average particle size of the order of $0.7 \pm 0.1 \mu\text{m}$.

PET (Figures 7a and 7b) presents similar result, and mG is homogeneously distributed on the surface, creating a physical barrier too. The features of the surface covered with mG does not show significant differences due to the deposited volume, from 0.4 to 0.8 mL. This is due to the uniform spread of the solution, thanks to the wettability of PET by NMP, indicating that the early distribution of mG leaves prevents them from further stacking and piling. Moreover, the larger volume and the uniform dispersion still preserved

the leaves suspended during the evaporation process until complete dryness, leading to thicker laid-down mG coating, characteristic of deposition governed by van der Waals forces among the leaves. The average size of graphene leaves on PET was also $0.7 \pm 0.1 \mu\text{m}$. The irregular morphology and packing due to scattered sequential deposition of the mG flakes precluded precise quantification of the number of particles per unit area of substrate.

In the case of the office paper, mostly comprised by cellulose fibers, the deposition of the graphene solution did not form a film on the fibrous and porous surface of this substrate after the drying process, according to SEM analysis (Figure 8a). The aggregate structure between the fibers of the paper treated with the dispersion does not show conclusive evidence of any graphene covering, either particles or agglomerations. Furthermore, no graphene coating is observed on the paper fibers. Even at higher magnifications (as shown in the Figures 8c and 8d, it is not possible to observe any significant difference between the paper with and without deposition of the graphene dispersion, though the

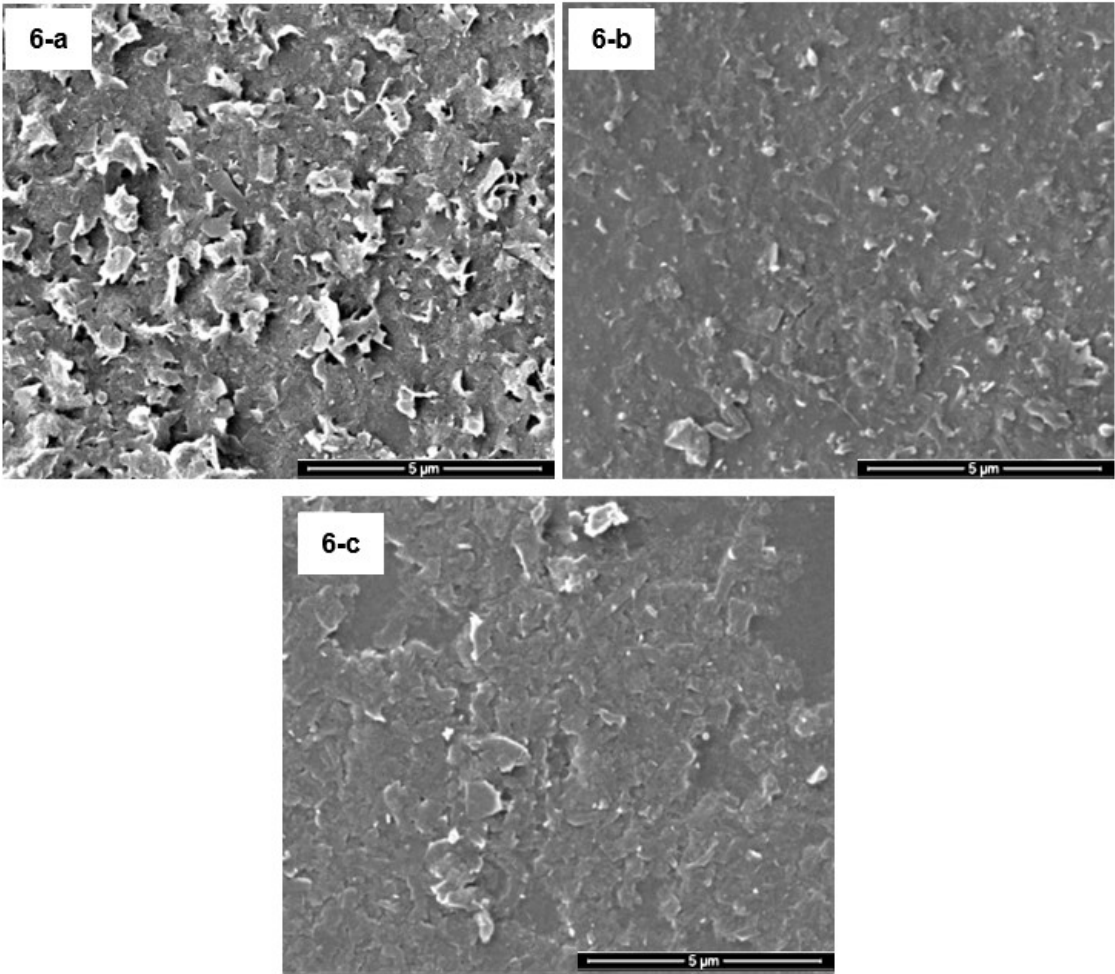


Figure 6. SEM images of cellophanes' top coating (25000X): a) with a well dispersed and non-parallel to surface graphene leaves; b) with 0.4 mL graphene-NMP solution; and c) with 0.8 mL graphene-NMP solution.

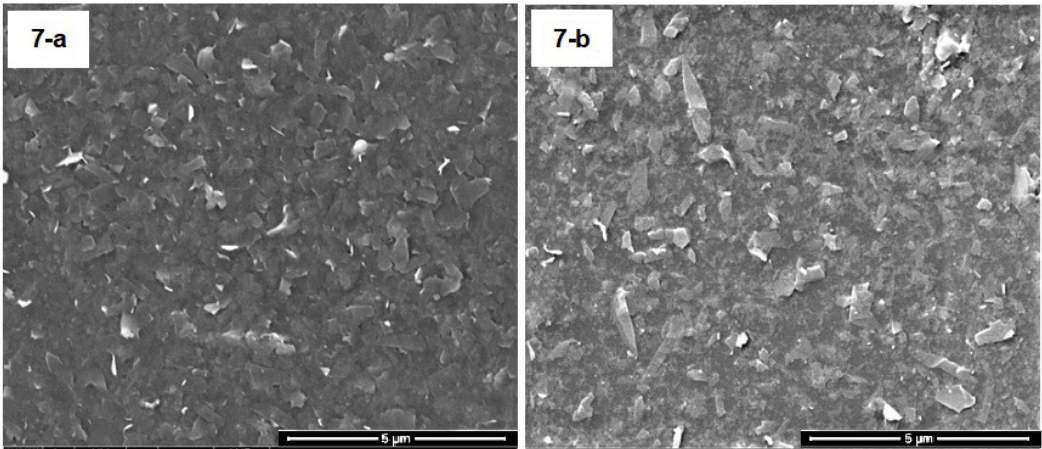


Figure 7. SEM images, at 25000 magnification, of PET coated by well-dispersed graphene leaves: a) with 0.4 mL and b) with 0.8 mL.

paper samples after treatment are essentially grayish-white indicating macroscopically the presence of carbon material.

Actually, there are many values reported for the surface energy of cellulose and regenerated cellulose,

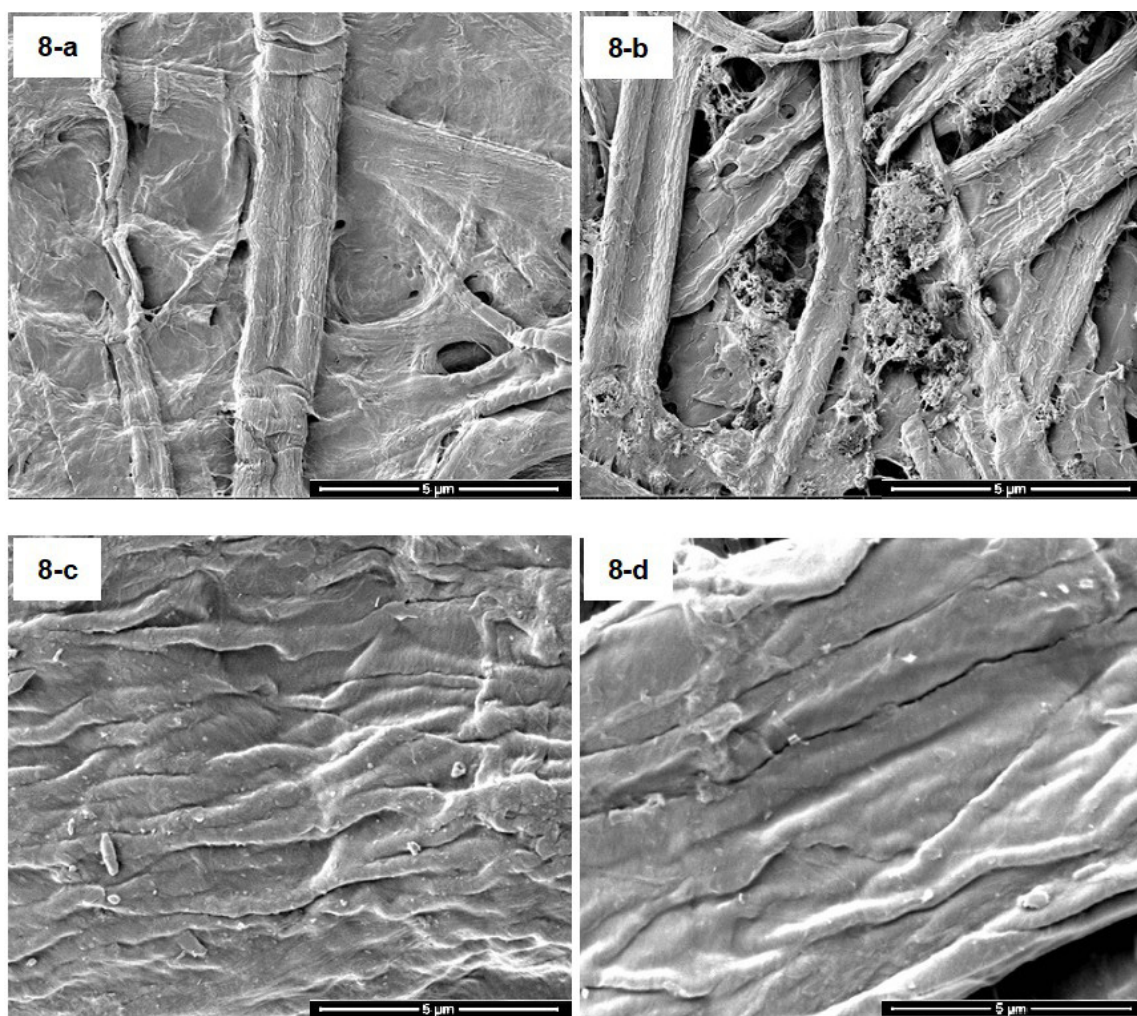


Figure 8. SEM images comparing original office paper at a) 2500X, b) 2500X, c) 25000X, and d) 25000X. Samples b) and d) were treated with mG.

like rayon and cellophane, because of its natural origin and processing stages until its transformation into foil or film. Cellulose is a semicrystalline natural polymer, comprised by hydrophobic and hydrophilic constitutive groups along the molecule that are preferentially exposed according to the contributing crystal plane. Thus, according to Yamane et al.³⁶, cellulose polymorphs show different surface energies for the main crystal planes ($1\bar{1}0$), (110), (200) and (020). Moreover, the diverse polymorphs display surface energies that can be as high as 178 mN/m for the crystal face ($1\bar{1}0$) of the polymorph Cell-II (determined by computer simulation), compared to those, much lower, of the plane (110), 101 mN/m and 62 mN/m for the polymorphs Cell-II and Cell-I_a, respectively.

The interfacial adhesion between graphene and polymeric substrates was tested according to ASTM F2252/F2252M-13³⁷. This standard finds widespread application in industries reliant on the printing or coating of flexible packaging, including the food and beverage, pharmaceutical, and consumer goods sectors. Briefly, a pressure-sensitive adhesive tape is applied

and, subsequently, removed to assess the adhesion strength of the applied ink or coating on the substrate. The extension of the detached ink or coating by the tape provides a qualitative measure of the adhesion quality. According to this standard, the results are exclusively qualitative.

The tape tests revealed a distinct contrast in the adhesion behavior of the mG-coated polymeric substrates. The graphene exhibited robust interfacial adhesion with PET and CEL, remaining fully intact after the application and removal of the adhesive tape. However, meticulous visual analysis of the LDPE films showed that the graphene layer was removed during the tape test; the removed graphene could be observed adhering to the adhesive tape. The same method was employed for the PET and CEL samples, but meticulous visual inspection of the film surface and the adhesive tape after application revealed neither the removal of the graphene layer nor the presence of graphene adhered to the tape. This indicates that the graphene coating on PET and CEL substrates demonstrated superior adhesion compared to the LDPE substrate (Figure 9).

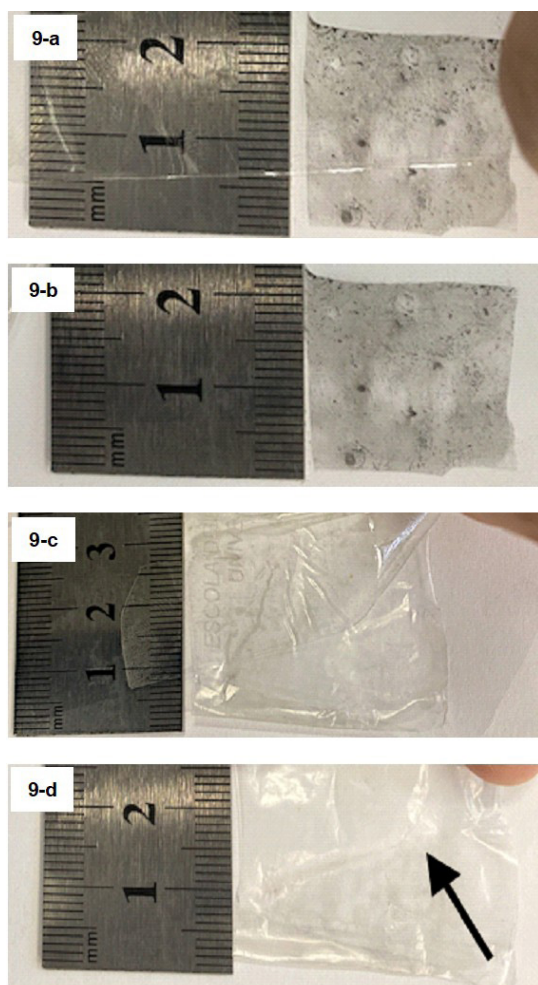


Figure 9. SEM images comparing original a) mG coated CEL film before tape test, b) mG coated CEL film after tape test, c) mG coated LDPE film before tape test, and d) mG coated LDPE film before tape test. The arrow indicates the region where mG was removed.

The results of some authors^{4,6,36,38-41} on the adhesion between graphene and a polymeric surface or interface are controversial, nonetheless it is governed by the secondary van der Waals interactions and by the particle sizes, defects, and number of layers of graphene, just to cite some elements, along with the dispersing solvent and the substrate characteristics. As noted, we cannot pre-establish the morphology of the coating based on a few variables. Paper and cellulose are chemically alike materials and presented very different results. Here, the roughness of the paper prevented the covering by the mG leaves, while in the case of CEL, the polar character of the NMP favored optimal dispersion on its surface, analogous to PET. In the case of LDPE, despite the graphene and the substrate being non-polar, the polar character of the solvent prevailed and was the determining factor for the poor surface spreading of mG.

4. Conclusions

The Raman spectra of mG deposited on the glass slides along with the comparison with the pristine graphite spectrum

indicate that the exfoliation process was successful, resulting in 2- to 5-layer graphenes. The mG dispersion in NMP is a good medium to be used in drip casting of polymer surfaces. Coatings comprised by graphene sheets with homogeneous particle sizes were successfully produced on CEL and PET substrates and may be a promising way to provide barrier and anti-static coatings in the packaging films. However, the same feature did not occur on the LDPE substrates, due to its non-polar character, and a large amount of uniform globular self-assemblies of mG, ca. 0.6 μm diameter, were observed on these surfaces due to repulsive forces between the substrate and the NMP dispersion. This is supported by the non-adhesion results of the graphene thin film coating on these substrates, as determined by the adhesive tape test. Even so, the LDPE transmittance spectrum in the visible range is still similar to those obtained for the other samples. On the office paper, the porous material absorbed the dispersion, and uniform coating was not evident, such as those observed on the other substrates, as the SEM images of this substrate with and without mG dispersion treatment are essentially unchanged. The unusual features of the graphene globular structures observed on LDPE film could point toward a way to prepare uniform submicron conductive particles.

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